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CATALYST LIFETIME TESTING FOR METHANOL SYNGAS CONDITIONING

Contract Number RAE-3-138442

Prepared by

Dr. Xianghong Zhao and Dr. Scott W. Cowley

February 28, 1994

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Colorado School of Mines

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Contract Number RAE-3-133442

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Preface

Biomass derived synthesis gas contains particulate matter, methane, and pyrolysis tars. All of these impurities must be removed before the gas can be used in a methanol synthesis reactor. A proprietary catalyst, DN-34, has been developed at Battelle Research Laboratories and two modified versions DN-34 have been developed at NREL. Before these catalysts can be considered for large scale experimentation, their durability and stability over an extended time must be determined. Preliminary lifetime studies of the DN-34, RE-1A, and RE-2A catalysts were conducted at CSM Surface and Catalyst Laboratories by Dr. Xianghong Zhao and Dr. Scott W. Cowley, and reported in this document.

Summary

Two 50 hour tests for DN-34 catalyst and two 8 hour tests for RE-1A and for RE-2A were made. The results showed that DN-34 and RE-1A has good activity for tar conversion. DN-34 and RE-1A catalysts gradually lost some activity for gas conversion during the testing period. In the first 8 hour runs of DN-34 and RE-1A, the activity of RE-1A was slightly higher than that of DN-34. DN-34 catalyst gradually lost activity for the synthetic tar conversion in about 30 hours. RE-2A catalyst did not show good activity for the synthetic tar conversion compared to RE-1A and DN-34. The activity of RE-2A for the mixture gas was about the same as the activities of RE-1A and DN-34 catalysts.

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Experimental

1.1 Materials

The materials used for the lifetime testing experiments and for calibration of the reactor system are:

* Gases (**Tables 1 and 2**)
* Liquids and solids (**Table 3**)

Table 1. Gas mixture (Matheson)

Gas	Mole Weight	Requested Mole%	Analysis Mole%
Hydrogen (H_2)	2	26.00	25.86
Carbon Monoxide (CO)	28	38.00	38.33
Methane (CH_4)	16	15.00	14.97
Carbon Dioxide (CO_2)	44	15.00	14.89
Ethylene (C_2H_4)	28	5.00	4.96
Acetylene (C_2H_2)	26	0.50	0.50
Ethane (C_2H_6)	30	0.50	0.49

Table 2. Pure gases

Gas	Mole Weight	Purity Mole%	Supplier
Ethylene (C_2H_4)	28	99.99	Linde
Acetylene (C_2H_2)	26	99.99	Scientific
Ethane (C_2H_6)	30	99.99	Scientific

Table 3. Aromatic compounds

Chemical	Purity (wt%)	Supplier
Benzene (C_6H_6)	99.9	Mallinckrodt
Toluene (C_7H_8)	99+	Mallinckrodt
Naphthalene ($C_{10}H_8$)	99.9	General Chemical

1.2 Catalyst Evaluation System

A two stage up-flow tubular reactor as shown in **Figure 1** was used for evaluating the catalysts' performance. The mixture gas flow rate was monitored by the gas flow rotameter. Separate syringe pumps were used to meter the water and synthetic tar flow rates. The liquids were vaporized and mixed with the mixture gas in the vaporizer. The mixture vapor was introduced into the catalytic bed. The catalytic reactor was made of a 1/2 inch O.D. quartz tube with a fused fretted quartz disk to support the catalyst bed. The product gases exited via a heated exit line and were sampled for gas chromatographic analysis. Two gas chromatographs were used in series. The first chromatograph Tracor 560 FID for analysis of unreacted synthetic tar was placed as close to the exit line as possible to avoid any condensation problems. The second on-line gas chromatograph Perkin Elmer Sigma 3B TCD was used to analyze the syngas leaving the catalyst bed.

1.3 Calibration of Gas Chromatograph (GC)

The analytical technique for determining the reactant conversion and product distribution was gas chromatography. This was supplemented by analysis of pure chemicals. This method helped to elucidate the chemical changes which the reactants underwent.

Aromatic hydrocarbons were analyzed on an on-line Tracor 560 Gas Chromatograph using a film ion detector (FID) and helium as the carrier gas. The Tracor 560 was equipped with a 3 meter packed column containing Supelco 10% SP-2100 on 80/100 mesh Supelcoport packing. The operating conditions for the Tracor 560 were as follows:

Temperatures 80/200°C
Time 0/20 minutes
Ramp rate 20°C/minute
Inject port 150°C
Detector 235°C

Gas product samples were analyzed on an on-line Perkin Elmer Sigma 3B gas chromatograph using a thermal conductivity detector (TCD). The carrier gas was 2% hydrogen and 98% helium. The Perkin Elmer Sigma 3B was equipped with a 3 meter stainless steel column containing

Porpak Q on 80-100 mesh Supelcoport packing. The operating conditions for the Perkin Elmer Sigma 3B were as follows:

Temperatures 80/150°C
Time 0/15 minutes
Ramp rate 20°C/minute
Inject port 125°C
Detector 235°C

All the identifiable reactants and products were separated effectively in these columns, see **Figures 2, 3 and 4**.

Calibrations of the FID and TCD in the GC were performed for liquid and gas reactants and products. The relative response weight factors (RRWF) for the aromatic hydrocarbons and gases are presented in **Tables 4 and 5**.

The RRWF values were determined by the method shown in *Zhao and Cowley, 1992*. Benzene and carbon dioxide were used as standard compounds for the Tracor 560 and the Perkin Elmer Sigma 3B RRWF determination respectively.

1.4 Calibration of Syringe Pumps and Oven

Sage Instruments Model 341A and 341B syringe pumps were used to pump the water and synthetic tar into the reactor. They were calibrated, the results can be fitted by two straight lines of different slopes.

The Lindberg Serial No. 800698 oven was used for heating the catalyst bed. It was calibrated. The isothermal zone is placed 11 inches from the top of the oven and was about 1.7 inches long.

1.5 Catalyst Testing Procedure

The following procedure was used to test the catalysts for this research:

1. Approximately 2.5cc of catalyst was added to the top of the fused fritted quartz disk in the quartz reactor tube.

2. The reactor tube which contained the catalyst was attached to the reactor system by swagelock connectors and graphite ferrules located at each end. The on/off valves upstream and downstream were opened.

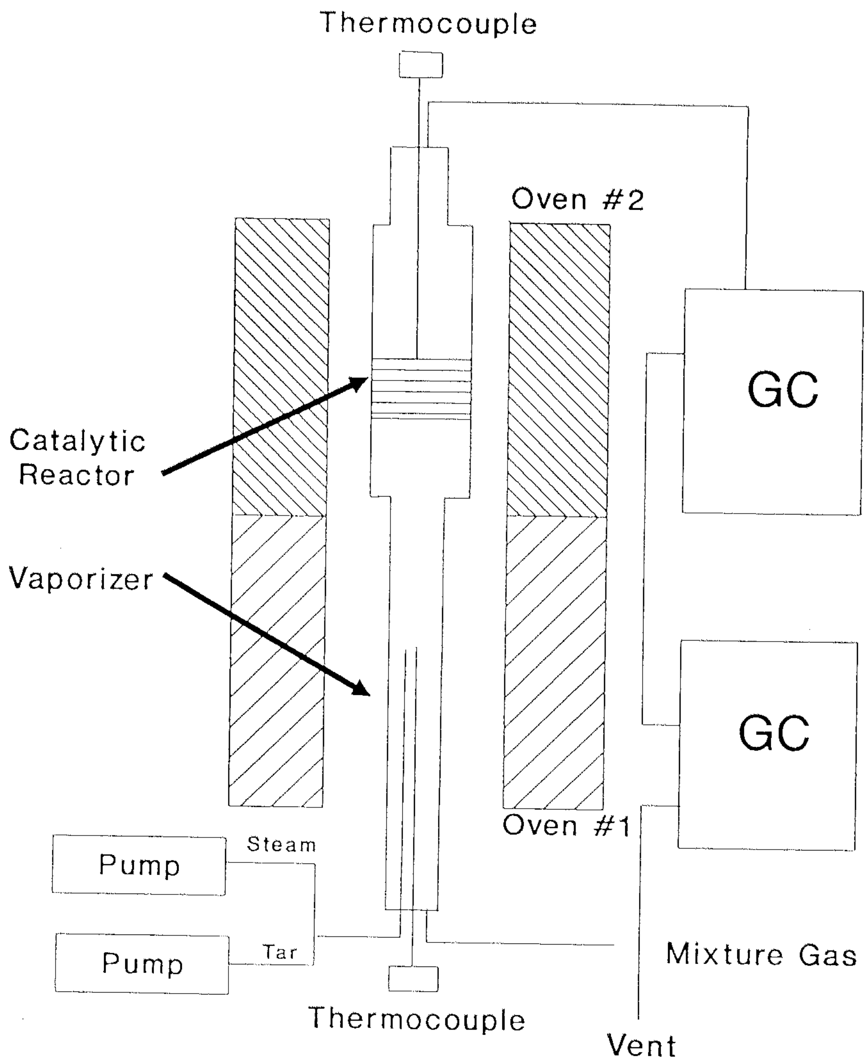


Figure 1. **Schematic of catalyst evaluation system**

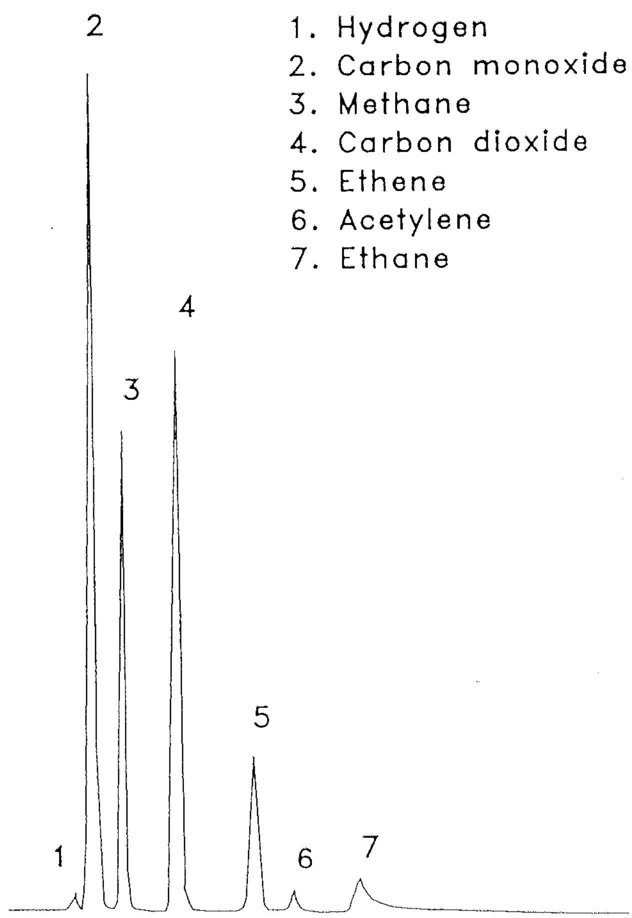


Figure 2. **Chromatogram of separation of hydrogen, carbon monoxide, methane, carbon dioxide, ethene, acetylene and ethane with Porpak Q on 80-100 mesh Supelcoport packing.**

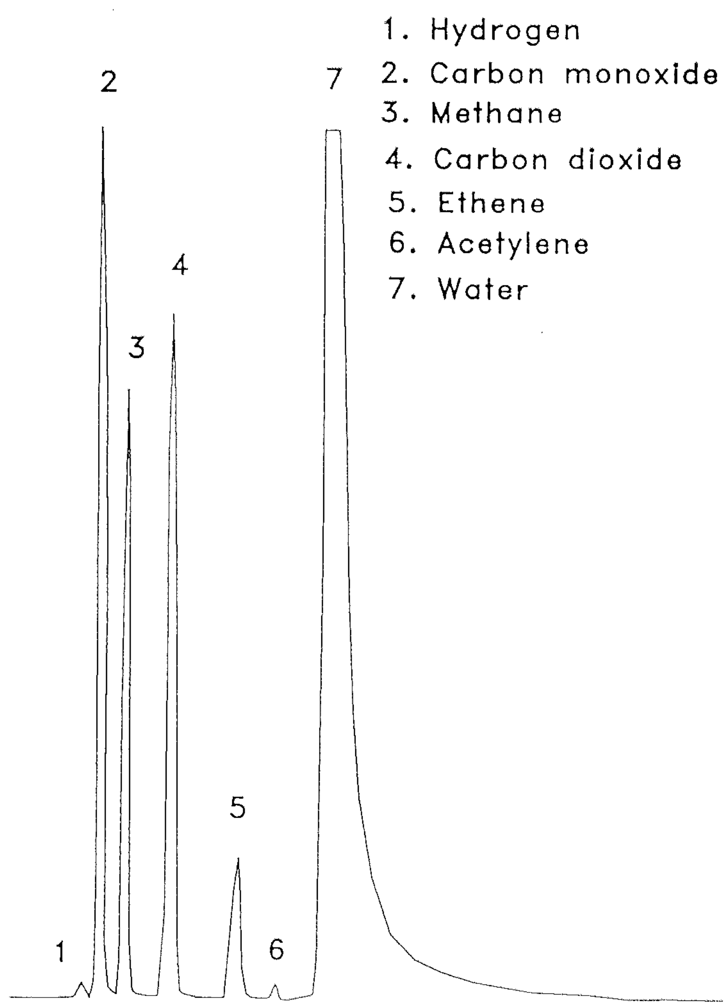


Figure 3. Chromatogram of separation of hydrogen, carbon monoxide, methane, carbon dioxide, ethene, acetylene, ethane and water with Porpak Q on 80-100 mesh Supelcoport packing.

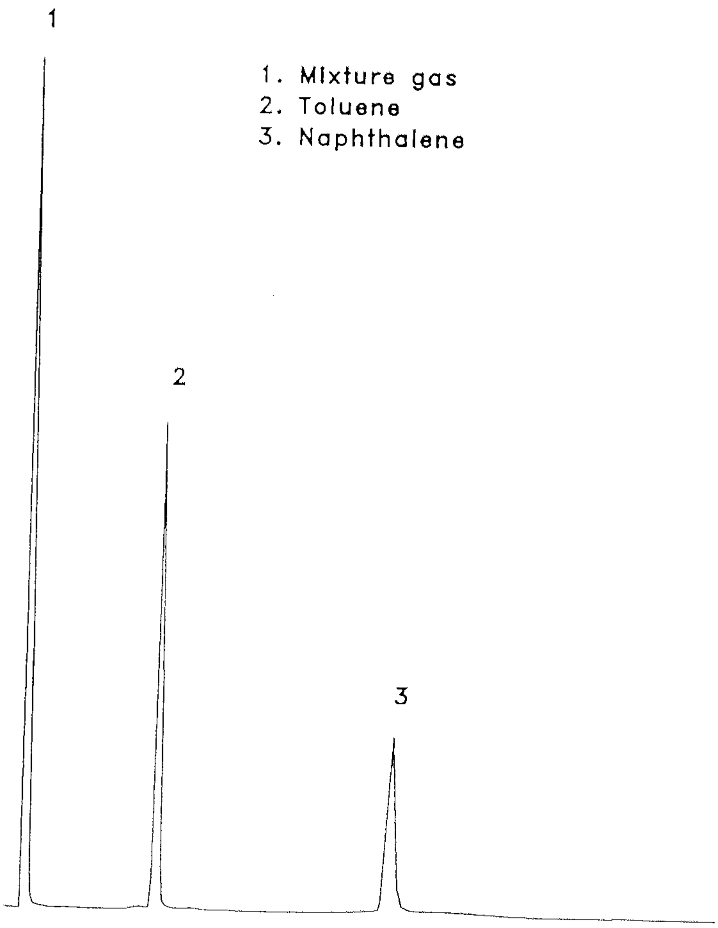


Figure 4. Chromatogram of separation of benzene, toluene, and naphthalene with Supelco 10% SP-2100 on 80-100 mesh Supelcoport.

Table 4. Retention time and relative response weight factors of Tracor 560 GC FID

Compound	Mole Weight	Retention Time (min.)	Relative Response Weight Factor (RRWF)
Benzene	78	3.1	0.78
Toluene	92	4.2	0.98
Naphthalene	128	10.3	1.10

Table 5. Retention time and relative response weight factors of Perkin Elmer Sigma 3B GC TCD

Compound	Mole Weight	Retention Time (min.)	Relative Response Weight Factor (RRWF)
Hydrogen (H_2)	2	1.1	2.41
Carbon Monoxide (CO)	28	1.3	0.31
Methane (CH_4)	16	1.7	0.25
Carbon Dioxide (CO_2)	44	2.3	0.44
Ethene (C_2H_4)	28	3.1	0.27
Acetylene (C_2H_2)	26	3.7	0.23
Ethane(C_2H_6)	30	4.5	0.04(?)
Steam (H_2O)	18	4.6	----

3. Helium was added to the reactor system until the outlet gas flow maintained about 50 cc of gas/cc of catalyst-min. The system was maintained at 1 atm. Leaks of the swagelock connectors were detected with bubble soap, and corrected.

4. Helium was switched off and mixture gas switched on. The leaks were detected again with a flammable gas detector and corrected.

5. The gas was switched from mixture to helium again. The system was purged with helium for about 1 hour in order to prevent pre-coking caused by the mixture gas used for the leak test. Helium flow rate was controlled at about 50 cc of catalyst/cc of catalyst-min.

6. The temperatures of the catalyst bed and the vaporizer were raised to 50°C over a 0.5 hour period. All the heating tapes on the gas outlet were turned on.

7. The temperatures of the catalyst bed and the vaporizer were raised to 150°C over an additional 0.5 hour period.

8. The water syringe pump was turned on when the temperatures of the catalyst bed and the vaporizer reached 150°C. The gas flow was approximately 50 cc of gas/cc of catalyst-min. The water flow rate was maintained at about 3.5 cc/hr.

9. The temperatures of the catalyst bed and the vaporizer were raised to 815° over a 2 hour period. The flows of gas and water were controlled at the same rate.

10. The water flow was decreased to 4 cc/hr. The mixture gas was turned on. The synthetic tar syringe pump was turned on at the same time. The flow rate was about 0.013 cc/hr. The outlet gas flow rate was decreased to 9 cc of gas/cc of catalyst-min.

11. The actual liquid flow rate was monitored and recorded by the change of level on the syringe. The outlet gas flow rate was maintained by periodically adjusting the mixture gas flow meter.

12. The reaction was allowed to continue for 50 hours at the same conditions. The outlet gas was analyzed each hour by two on-line GC instruments.

13. After the experiment was finished, the power to the liquid pumps, the catalyst bed and the vaporizer was shut off. The mixture gas was switched to helium to flush the system; its flow rate was approximately 10 cc/min. The helium was left flowing through the system overnight.

14. The outlet heating tapes were turned off the following day. The reactor tube was removed. The catalyst was pushed out from the reactor tube. It will be placed in a labeled vial and returned to NREL.

1.6 Feedstocks

The synthetic tar tested in this study was 10 wt% naphthalene in toluene. The density of the solution was 0.8241. The composition of the gas mixture used in this study is given in **Table 1**. The ideal catalyst should totally steam reform the toluene and naphthalene to produce carbon dioxide and hydrogen with a minimum amount of coke. Naphthalene contains two aromatic rings. It is the simplest condensed aromatic compound. These fundamental studies of naphthalene can help in studying and understanding other more advanced condensed aromatic and related compounds.

1.7 Reaction Conditions

All experiments were performed at the specified operating conditions such as catalyst bed temperature, system pressure, feedstock composition and flow rate. The gas hourly space velocity was 2000 cc of gas/cc of catalyst-hr (at 815°C, 1 atm) or 9 cc of gas/cc of catalyst-min (at STP). The water flow rate was 0.45 cc/hr (0.4 cc/hr specified), and the synthetic tar flow rate was 0.0102 cc/hr (0.013 cc/hr specified), both at STP. The volume of catalyst used for each test was 2.5 cc (approximately 2 grams of DN-34). The concentration of the reactant was 0.2 mole% of synthetic tar (toluene + naphthalene), 40 mole% of steam, and 59.8 mole% of the mixture gas.

Section 2
Experimental Results and Discussion

2.1 Evaluation of Catalysts

Two 50 hour tests for DN-34 catalyst and two 8 hour tests for RE-1A and RE-2A respectively were made. The results showed that DN-34 and RE-1A had good activity for tar conversion. In the first 8 hour runs of DN-34 and RE-1A, the activity of RE-1A for the synthetic tar conversion was slightly (about 2 mole%) higher than that of DN-34.

2.2 Reactor Calibration Tests

In order to evaluate each new catalyst, three individual 6 hour period blank runs (without catalyst, at the same reaction conditions) were made. The results showed that about 90 mole% of toluene was steam reformed to form benzene and methane, and about 9 mole% of benzene was steam reformed to form carbon monoxide or carbon dioxide. Since a quartz tube was used, wall reactions were kept at a minimum. The reactions observed were likely thermal in nature. It is recommended that the thermodynamic values of the thermal reactions be determined in the near future.

2.3 Life Time Tests for DN-34 Catalyst

Two identical 50 hour runs were made for DN-34 catalyst, designated as **Run-F02-94** and **Run-D27-93**. The concentration of each compound in the mixture gas changed from initial conditions as presented in **Table 6**. After the initial three hours, the concentrations of the hydrogen and carbon dioxide linearly decreased in time, and carbon monoxide, acetylene, and ethylene linearly increased in time, while methane was constant, see **Appendix A, Figures 1-8**.

Some toluene and naphthalene were converted into CO or CO_2, H_2, and benzene. The conversions of toluene and naphthalene were 100 mole% in the 50 hours. The conversion of benzene (a reforming product) gradually decreased from 94 to 90 mole% in the first 30 hours, then rapidly decreased from 90 to 80 mole%, and finally decreased from 80 to 75 mole% until the end of the 50 hour test, see **Appendix A, Figures 17-20**.

The catalyst DN-34 gradually lost some activity during the testing period. At the end of the experiment the catalyst and the reactor tube showed definite signs of coking as evidenced by a dark black color.

Table 6. Effect of time on gas product distribution for DN-34

Tested Material	DN-34 (2 grams, 2.5cc)		
Feed Composition	10 wt% naphthalene + 90 wt% toluene (Density=0.8241)		
Gas Hourly Space Velocity (GHSV)	2000 cc gas/cc catalyst-hr (815°C) 9 cc gas/cc catalyst-min(25°C)		
Conditions	1 atm and 815°C		
Time on Stream (hr)	0	3	50
Component	Mole Percent		
Hydrogen	26.1	29.6	25.2
Carbon Monoxide	38.2	18.2	22.5
Methane	15.1	16.7	17.9
Carbon Dioxide	15.1	33.4	30.9
Ethylene	5.0	1.8	3.1
Acetylene	0.5	0.3	0.4

Based on the observed products the following reaction sequence for steam reforming of toluene, benzene and naphthalene can be proposed:

Syngas reactions

1. $CO + H_2O = CO_2 + H_2$

2. $CO + 3H_2 = CH_4 + H_2O$

3. $CH_4 + H_2O = CO + 3H_2$

4. $C_2H_4 + 2H_2O = 2CO + 4H_2$

5. $C_2H_2 + 2H_2O = 2CO + 3H_2$

6. $C_2H_6 + 2H_2O = 2CO + 5H_2$

Toluene and benzene steam reforming

1. Hydrodealkylation:

$$C_6H_5\text{-}CH_3 + H_2 = C_6H_6 + CH_4$$

2. Steam dealkylation:

$$C_6H_5\text{-}CH_3 + H_2O = C_6H_6 + CO + 2H_2$$

3. Total steam degradation:

$$C_6H_5\text{-}CH_3 + 7H_2O = 7CO + 11H_2$$

$$C_6H_6 + 6H_2O = 6CO + 9H_2$$

Naphthalene steam reforming

1. Ring opening:

$$C_{10}H_8 + 4H_2O = C_6H_6 + 4CO + 5H_2$$

2. Total degradation:

$$C_{10}H_8 + 10H_2O = 10CO + 14H_2$$

At around 33 hours (**Figure 1**), a water syringe leak was found at the same time as the concentrations deviated from linear behavior. The leak was corrected immediately. The results suggest that the flow rate of water was important to the activity of the catalyst. A study of the effects of water flow rate on the catalyst's activity are recommended for the future.

To explain the deviations in linearity in the curves in **Figure 5**, a heating tape was found to be out of order on the gas exit line next to the second GC used to analyze the products, resulting in condensation of the tar components in the reaction exit line. The broken heating tape was changed immediately.

2.4 Testing of RE-1A catalyst

An 8 hour period test was made at the desired conditions for the RE-1A catalyst, designated as **Run-F08-94**. The concentration of the each component in the mixture gas changed as shown in the **Table 7**.

Table 7. Effect of time on gas product distribution for RE-1A

Tested Material	RE-1A (2.6160 grams, 2.5cc)		
Feed Composition	10 wt% naphthalene + 90 wt% toluene (Density=0.8241)		
Gas Hourly Space Velocity (GHSV)	2000 cc gas/cc catalyst-hr (815°C) 9 cc gas/cc catalyst-min(25°C)		
Conditions	1 atm and 815°C		
Time on Stream (hr)	0	3	8
Component	Mole Percent		
Hydrogen	25.1	28.2	28.5
Carbon Monoxide	38.2	17.6	18.3
Methane	15.1	17.8	17.5
Carbon Dioxide	15.1	34.4	33.7
Ethylene	5.0	2.0	2.0
Acetylene	0.5	0.0	0.0

After the initial three hours, the concentrations of hydrogen and carbon dioxide linearly decreased in time, and carbon monoxide, ethene, and acetylene linearly increased in time, while methane was constant, see **Appendix A, Figures 9-12**.

The synthetic tar had a good conversion with RE-1A catalyst. Benzene was 97 mole% converted at the third tested hour, and remained constant during experiment. Toluene and naphthalene were 100 mole% converted during the 8 hour experiment period, see **Appendix A, Figures 21 and 22**. At the end of the experiment the catalyst did not show significant signs of coking.

2.5 Testing of RE-2A Catalyst

The RE-2A catalyst was tested for 8 hours, designated as **Run-F14-94**. This catalyst did not show good activity for the synthetic tar conversion compared to the RE-1A and DN-34 catalysts. The concentration of the mixture gas was about the same as RE-1A and DN-34, see **Appendix A, Figures 13-16**. The concentration of the mixture gas and the conversion of the synthetic tar are shown in **Tables 8 and 9**.

Table 8. Effect of time on gas product distribution for RE-2A

Tested Material	RE-2A (2.2015 grams, 2.5cc)		
Feed Composition	10 wt% naphthalene + 90 wt% toluene (Density=0.8241)		
Gas Hourly Space Velocity (GHSV)	2000 cc gas/cc catalyst-hr (815°C) 9 cc gas/cc catalyst-min(25°C)		
Conditions	1 atm and 815°C		
Time on Stream (hr)	0	3	8
Component	Mole Percent		
Hydrogen	26.1	29.5	28.5
Carbon Monoxide	38.2	15.4	16.8
Methane	15.1	17.3	17.4
Carbon Dioxide	15.1	35.5	34.8
Ethylene	5.0	2.3	2.2
Acetylene	0.5	0.0	0.3

Table 9. Effect of time on synthetic tar conversion for RE-2A

Tested Material	RE-2A (2.2015 grams, 2.5cc)		
Feed Composition	10 wt% naphthalene + 90 wt% toluene (Density=0.8241)		
Gas Hourly Space Velocity (GHSV)	2000 cc gas/cc catalyst-hr (815°C) 9 cc gas/cc catalyst-min(25°C)		
Conditions	1 atm and 815°C		
Time on Stream (hr)	3	5	8
Component	Mole Percent Converted		
Benzene	83	64	56
Toluene	82	78	70
Naphthalene	80	77	61

The activity of RE-2A for the tar conversion was lost very rapidly, see **Appendix A, Figures 23 and 24**. At the end of the experiment, the catalyst showed signs of coking as indicated by a dark gray color.

2.6 Conclusions

The RE-1A and DN-34 catalysts had good activity for the synthetic tar conversion. The activity of RE-1A was slightly higher than that of DN-34. A 50 hour lifetime test for RE-1A is recommended. Based on the results we obtained, to evaluate a catalyst's activity and selectivity, studies for each single component with the best catalyst selected are recommended.

2.7 Future Recommendations

Since an internal standard for accurately monitoring changes in the gas composition was lacking in this study, 5% argon in the gas mixture is required in the future.

Based on the results observed, the concentration of hydrogen did not show a balanced mass increase compared to carbon monoxide and carbon dioxide. Therefore, the accuracy of hydrogen analysis was a matter of concern. This will be determined and corrected in the near future.

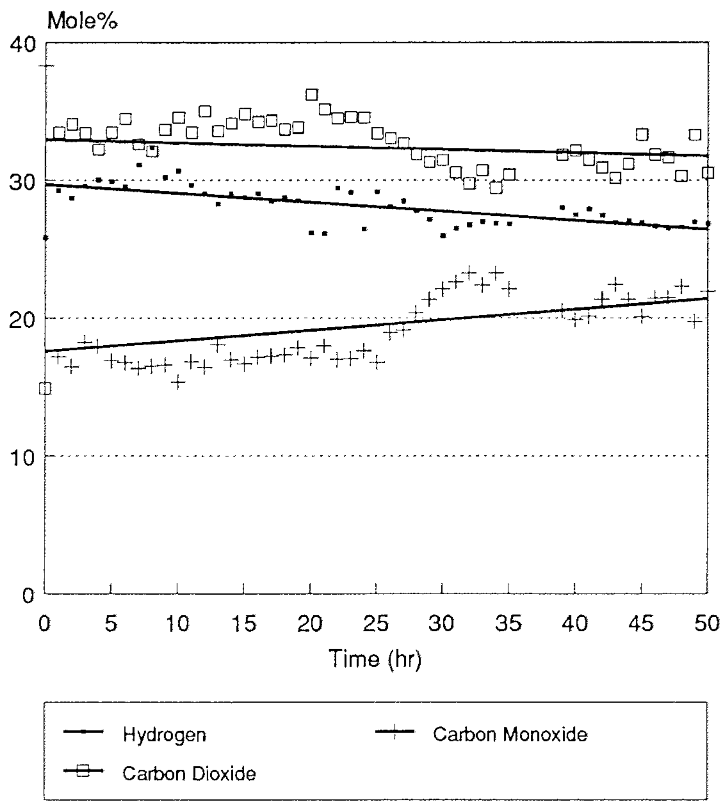
In order to more accurate evaluate the catalyst's activity, a by-pass next to the catalytic reactor tube is necessary in the future.

REFERENCES

Zhao, X. and Cowley, S. W. (1992). "Preparation, Characterization and Testing of Catalysts for Use in the Hydrotreatment of Model Lignin Feedstocks." NREL's final report.

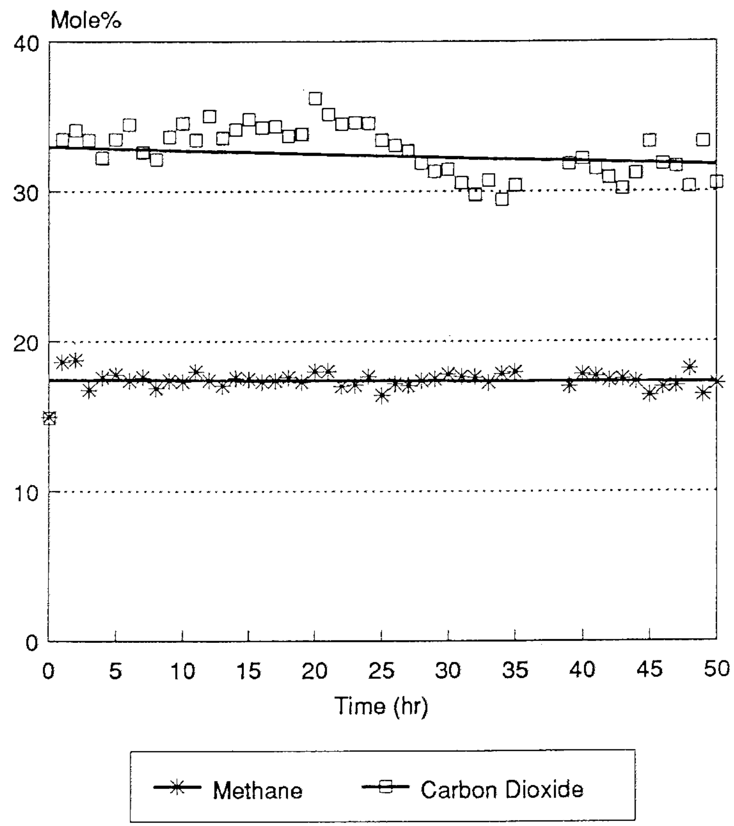
Appendix A

Figure 1. Change in carbon dioxide, carbon monoxide and hydrogen with time. Fifty hour test using DN-34.



Run-F02-94

Figure 2. Change in methane and carbon dioxide with time. Fifty hour test using DN-34.



Run-F02-94

Figure 3. Change in ethene and carbon monoxide with time. Fifty hour test using DN-34.

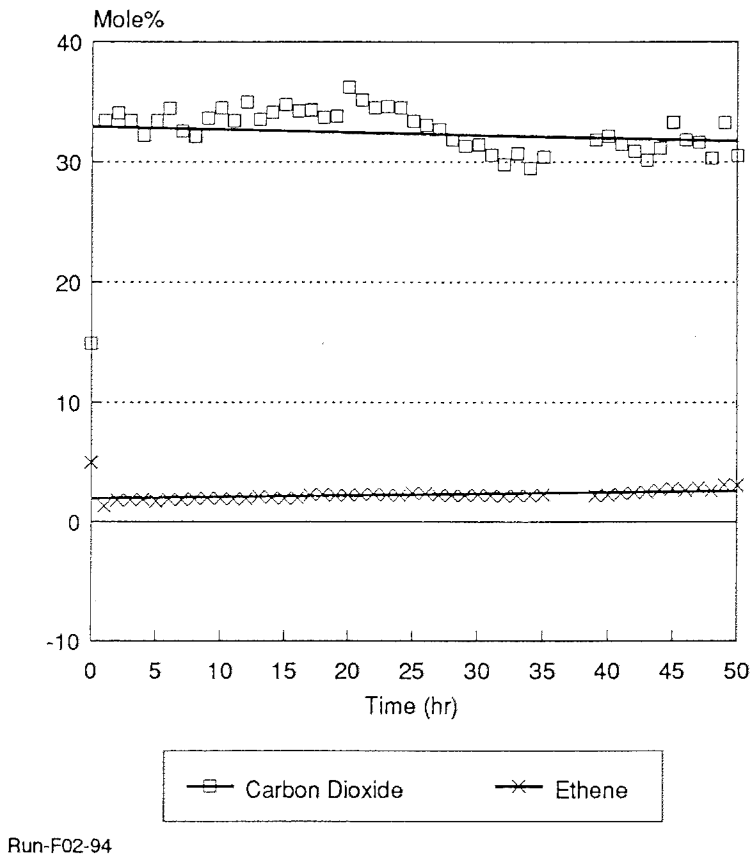


Figure 4. Change in ethene and acetylene with time. Fifty hour test using DN-34.

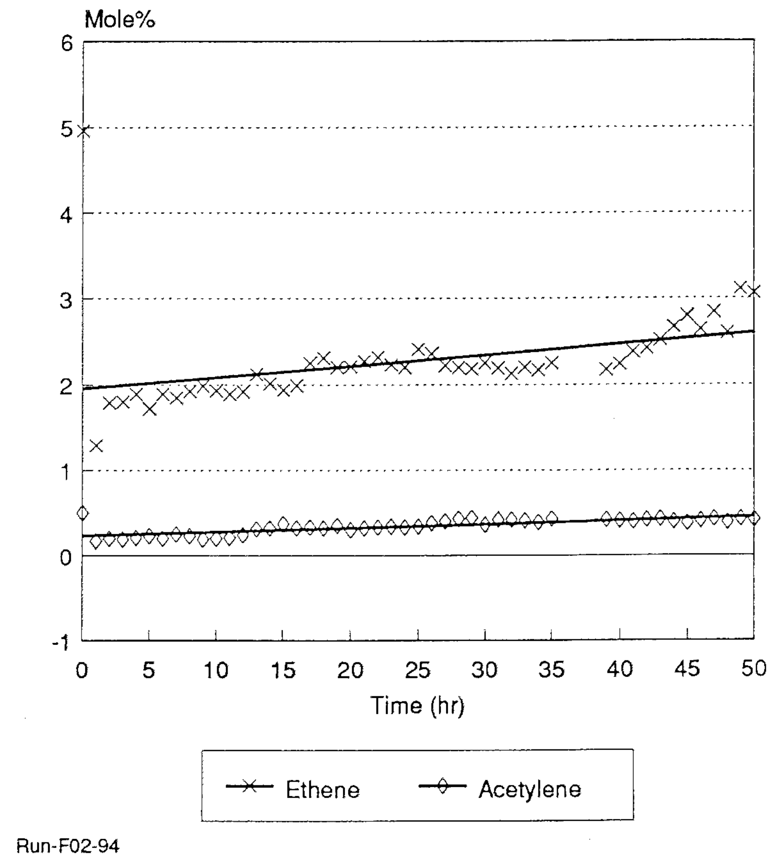
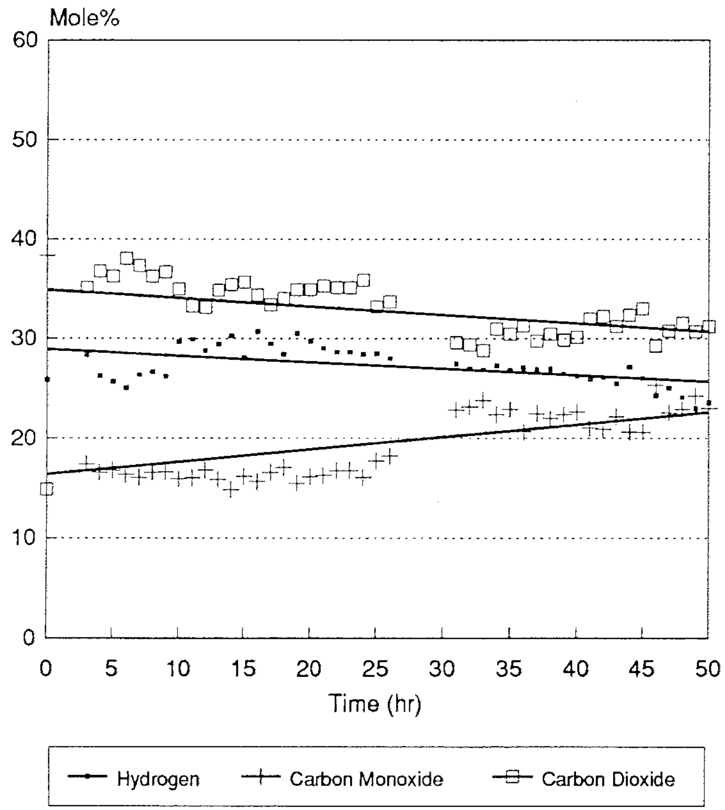
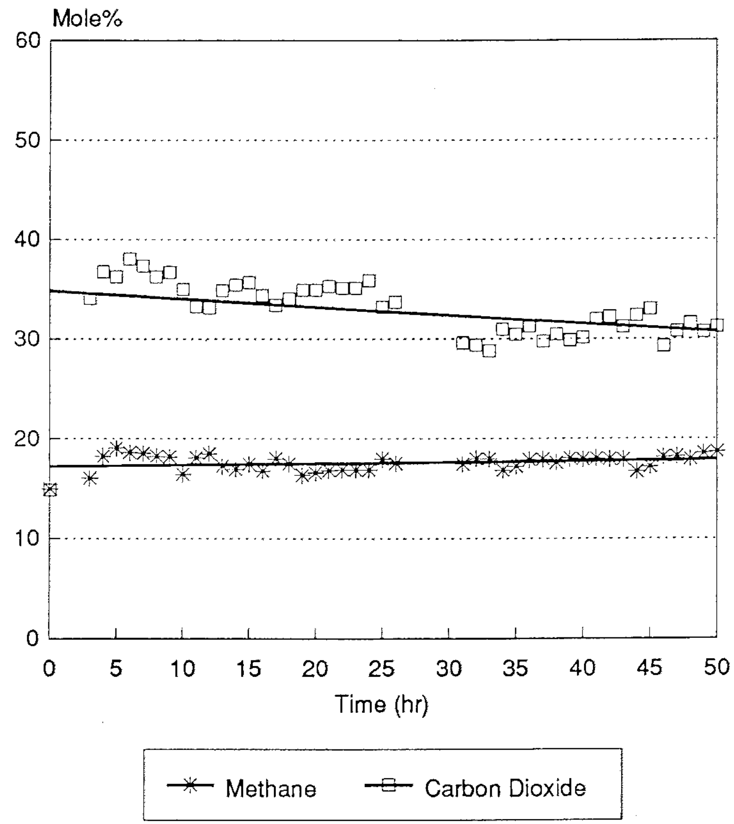


Figure 5. Change in carbon dioxide, carbon monoxide and hydrogen with time. Fifty hour test using DN-34



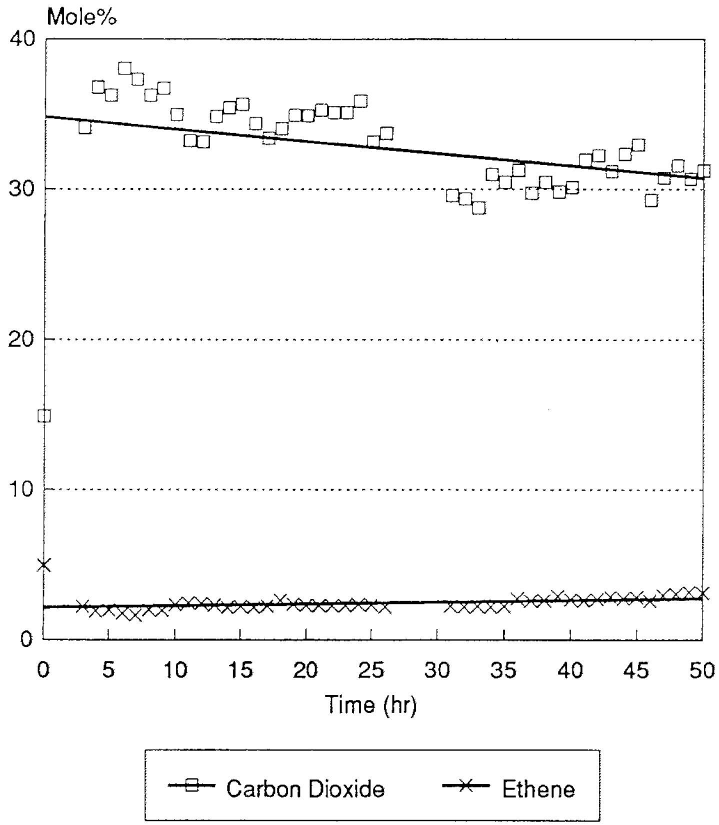
Run-D27-93

Figure 6. Change in carbon dioxide and methane with time. Fifty hour test using DN-34



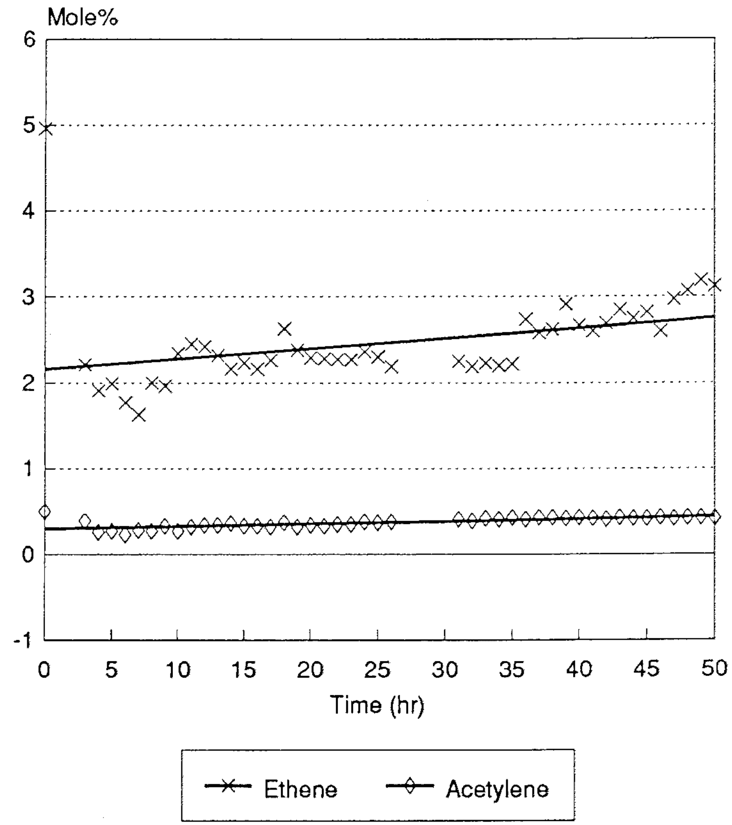
Run-D27-93

Figure 7. Change in carbon dioxide and ethene with time.
Fifty hour test using DN-34



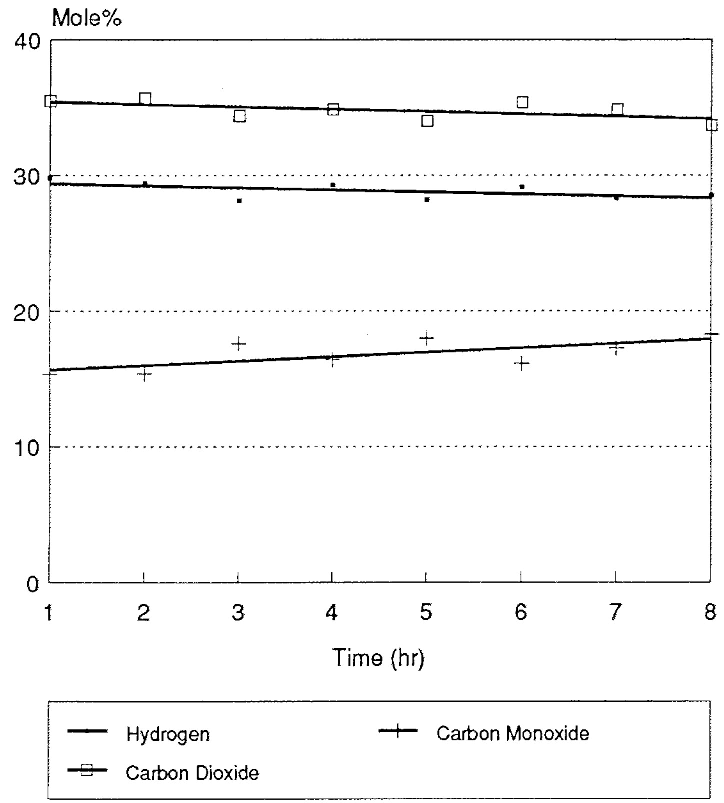
Run-D27-93

Figure 8. Change in ethene and acetylene with time
Fifty hour test using DN-34



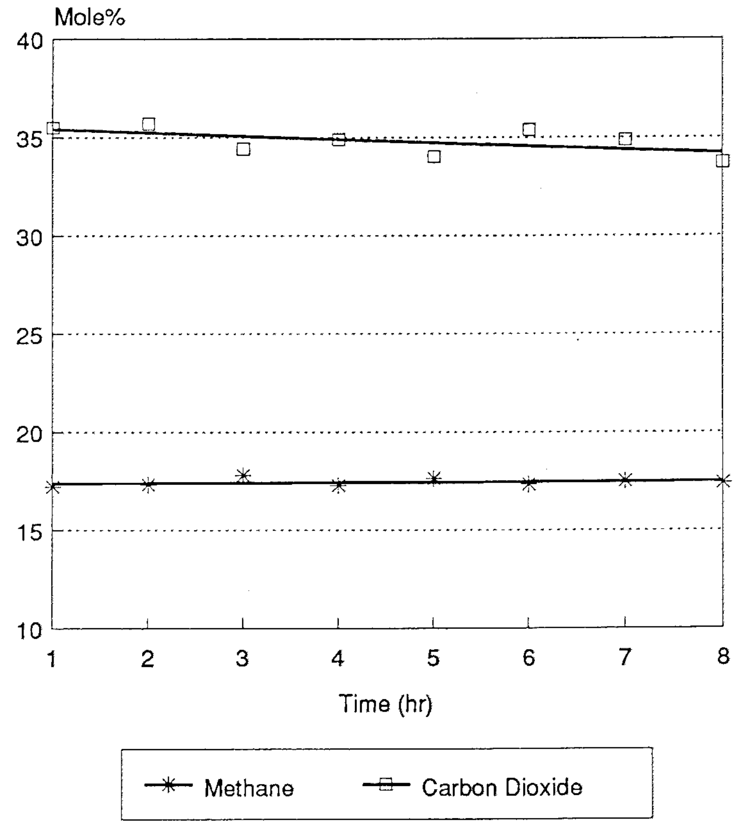
Run-D27-93

Figure 9. Change in carbon dioxide, carbon monoxide and hydrogen with time. Eight hour test using RE-1A.



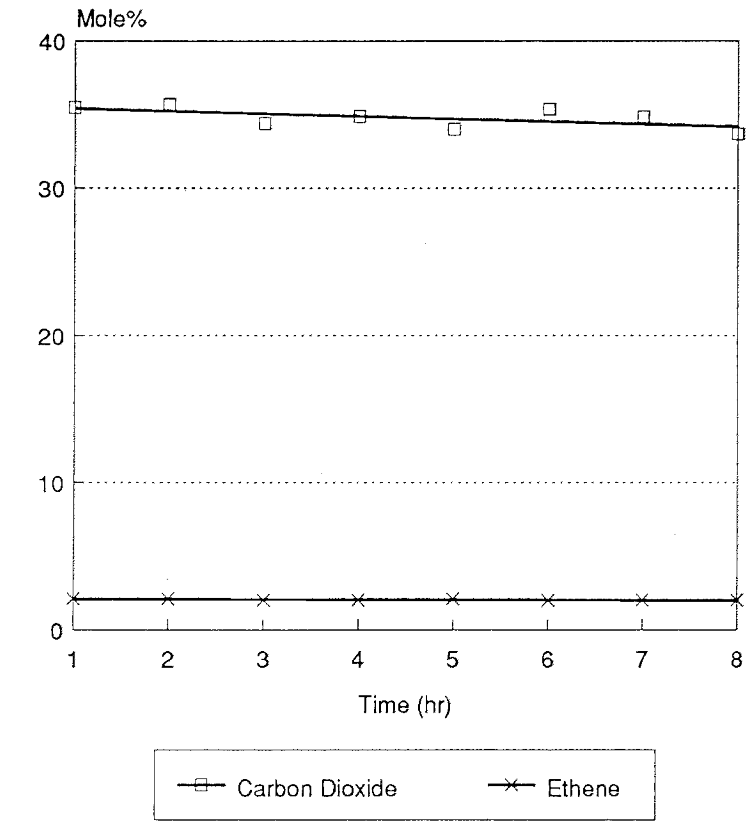
Run-F08-94

Figure 10. Change in carbon dioxide and methane with time. Eight hour test using RE-1A.



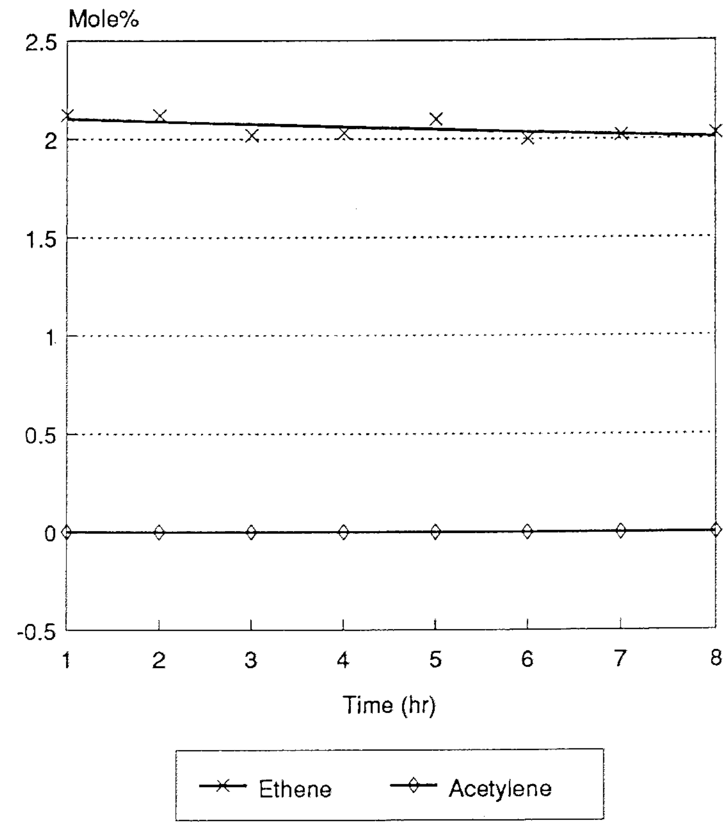
Run-F08-94

Figure 11. Change in carbon dioxide and ethene with time.
Eight hour test using RE-1A.



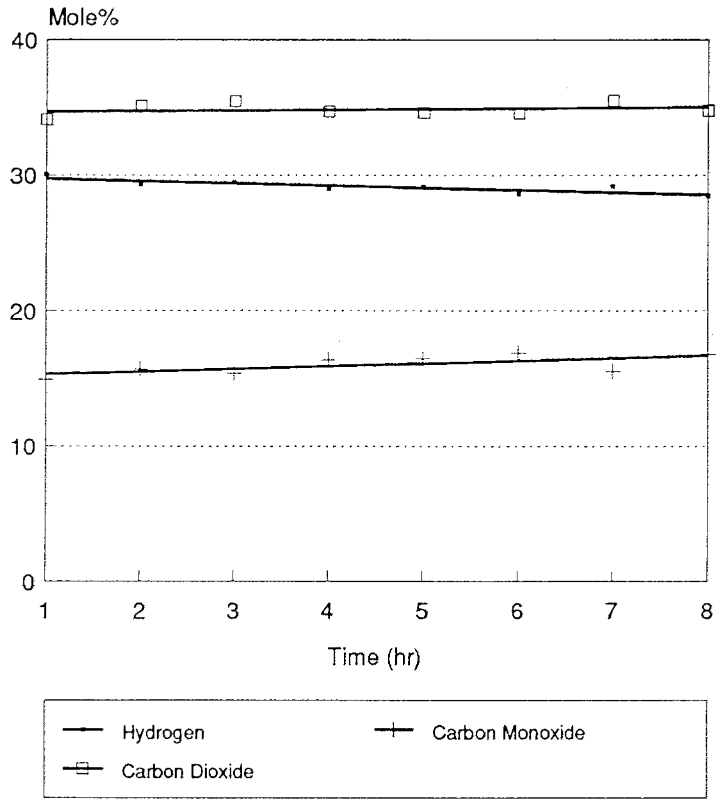
Run-F08-94

Figure 12. Change in ethene and acetylene with time
Eight hour test using RE-1A.



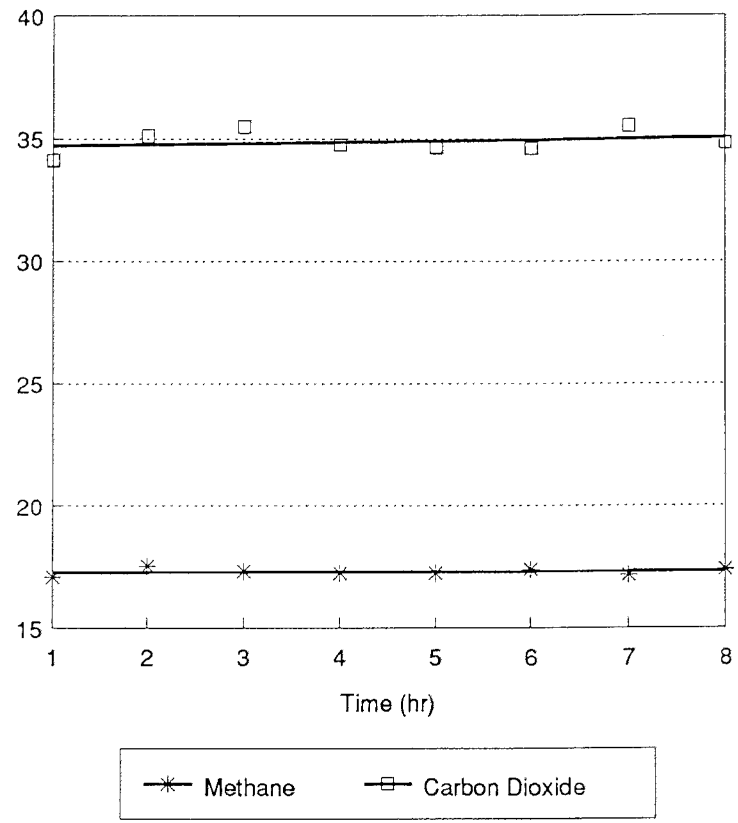
Run-F08-94

Figure 13. Change in carbon dioxide and carbon monoxide and hydrogen with time. Eight hour test using RE-2A.



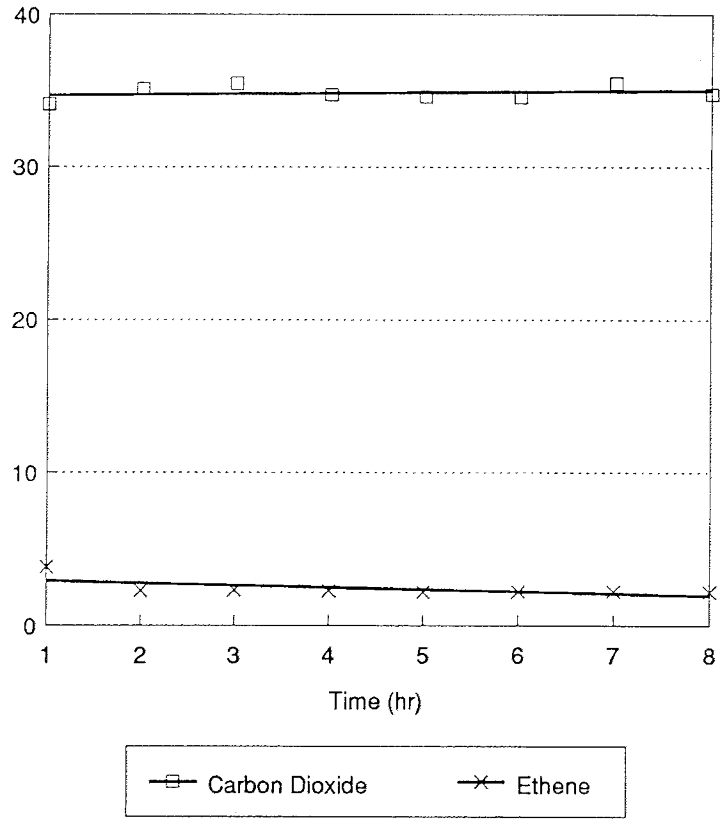
Run-F14-94

Figure 14. Change in carbon dioxide and methene with time Eight hour test using RE-2A.



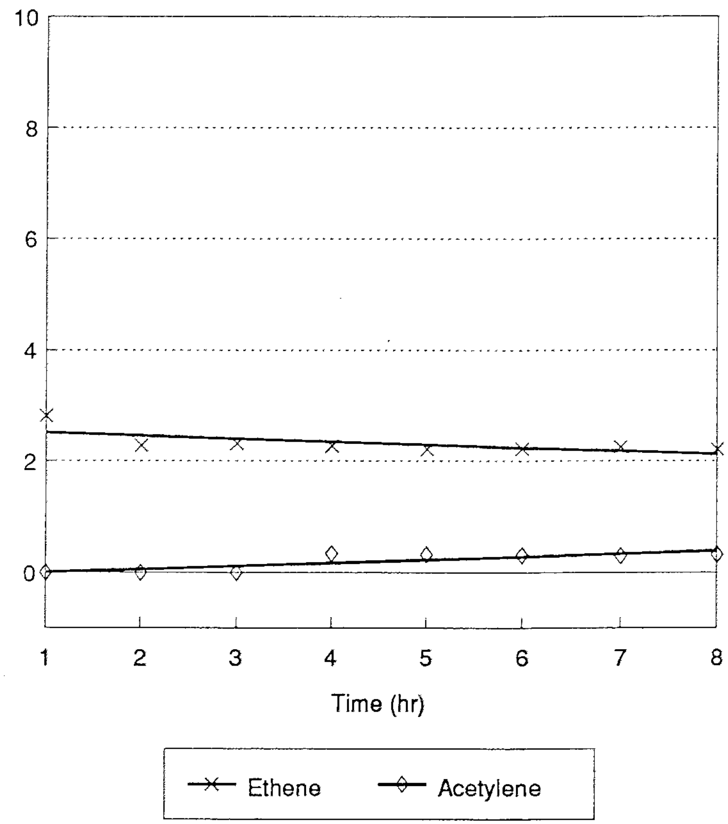
Run-F14-94

Figure 15. Change in carbon dioxide and
ethene with time
Eight hour test using RE-2A.



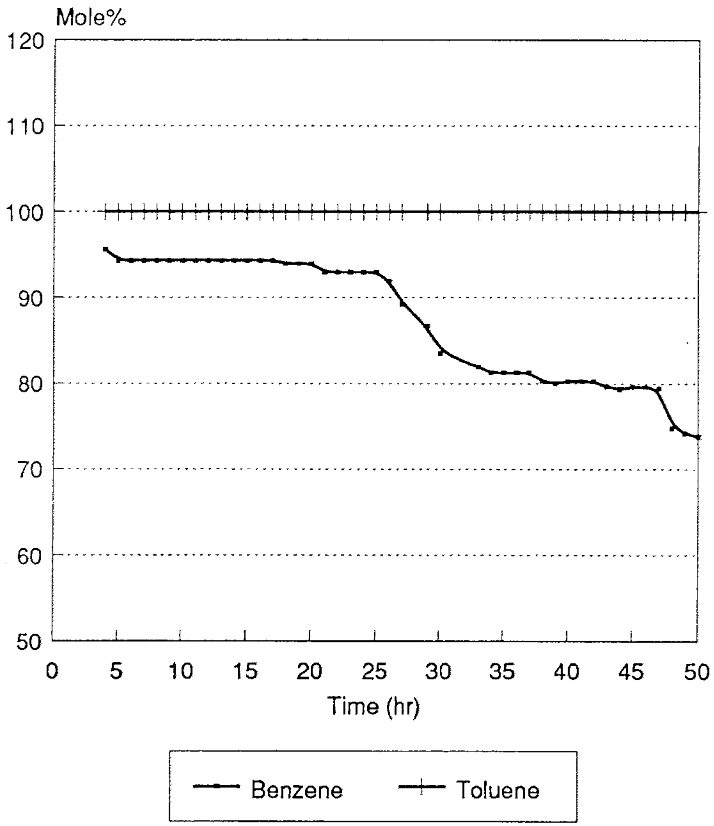
Run-F14-94

Figure 16. Change in acetylene
ethene with time
Eight hour test using RE-2A.



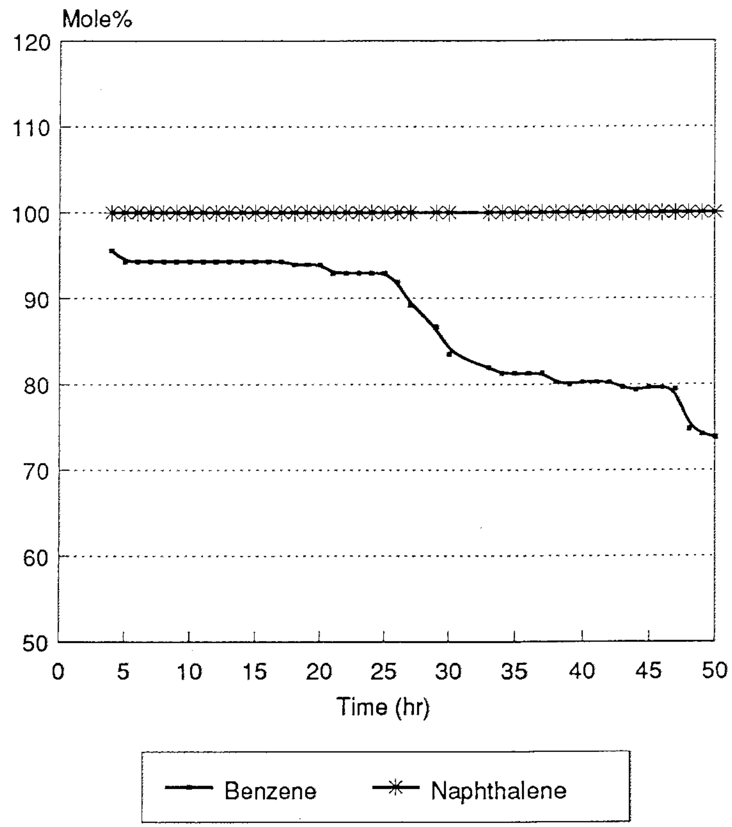
Run-F14-94

Figure 17. Change in benzene and toluene conversion with time. Fifty hour test using DN-34



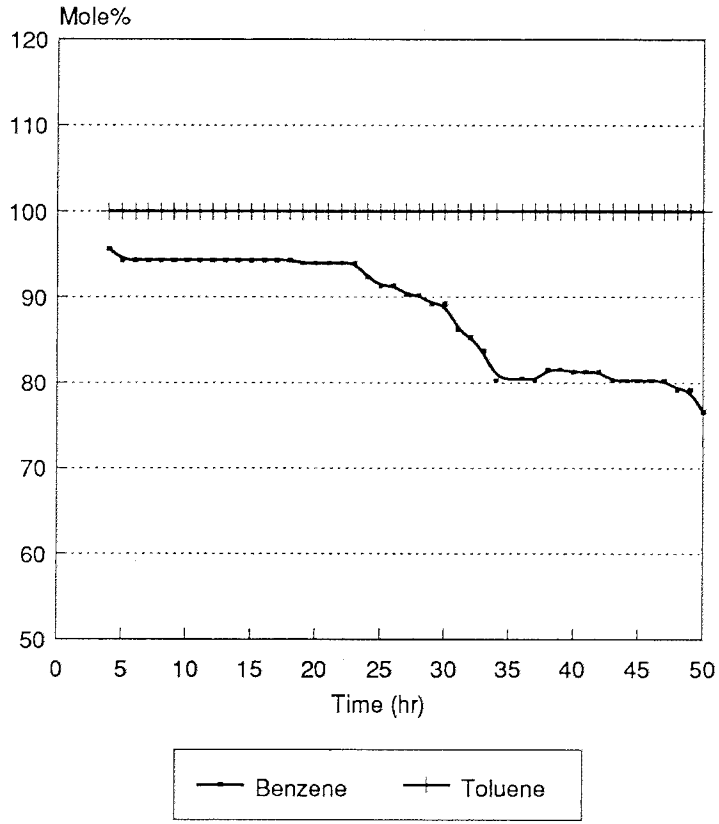
Run-D27-93

Figure 18. Change in benzene and naphthalene conversion with time. Fifty hour test using DN-34



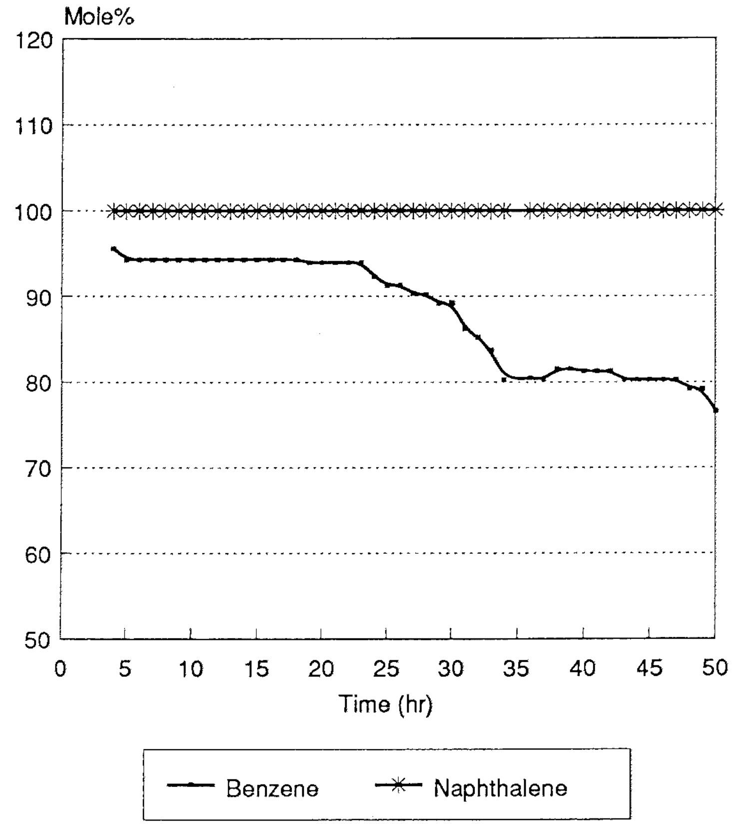
Run-D27-93

Figure 19. Change in benzene and toluene conversion with time. Fifty hour test using DN-34



Run-F02-94

Figure 20. Change in benzene and naphthalene conversion with time. Fifty hour test using DN-34



Run-F02-94

Figure 21. Change in benzene and toluene conversion with time
Eight hour test using RE-1A

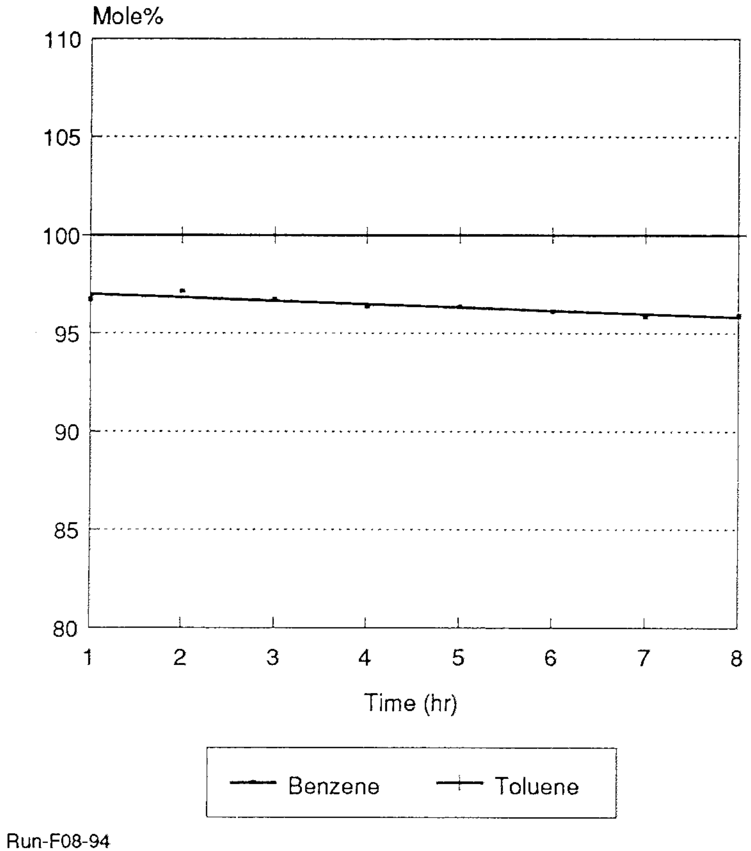


Figure 22. Change in benzene and naphthalene conversion with time.
Eight hour test using RE-1A

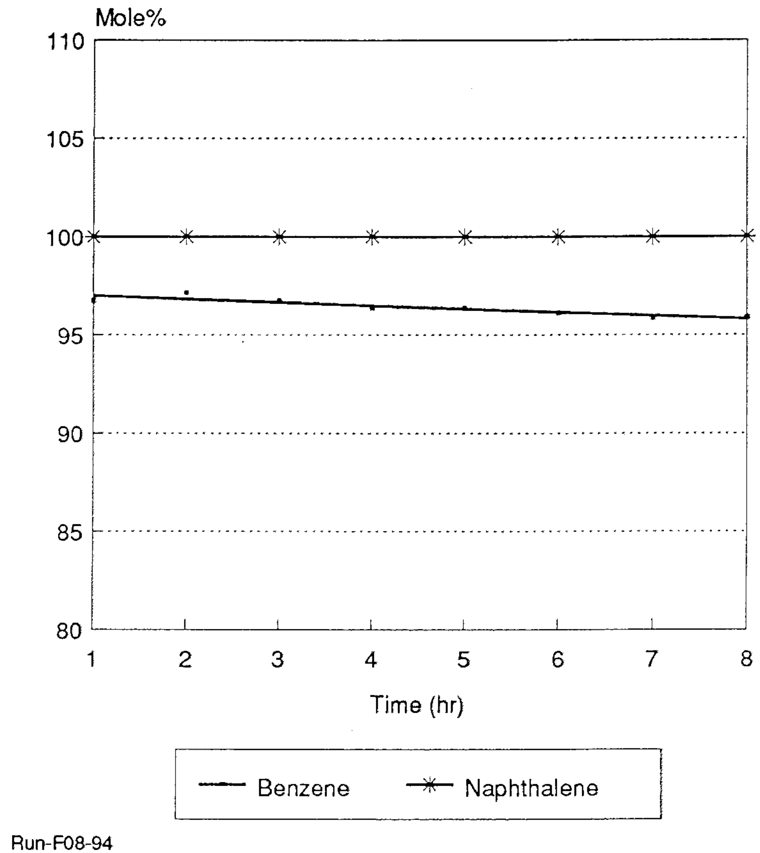
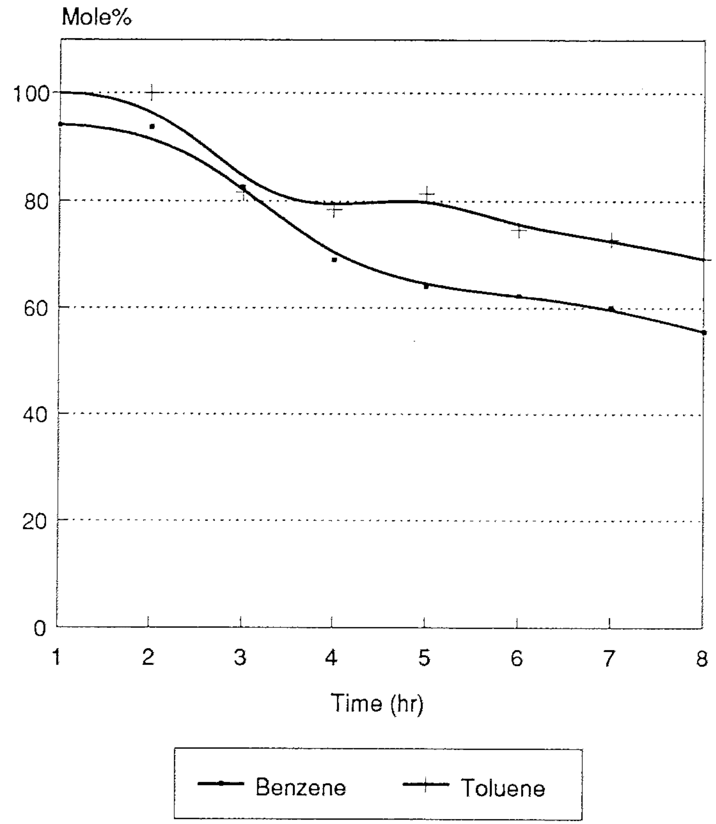
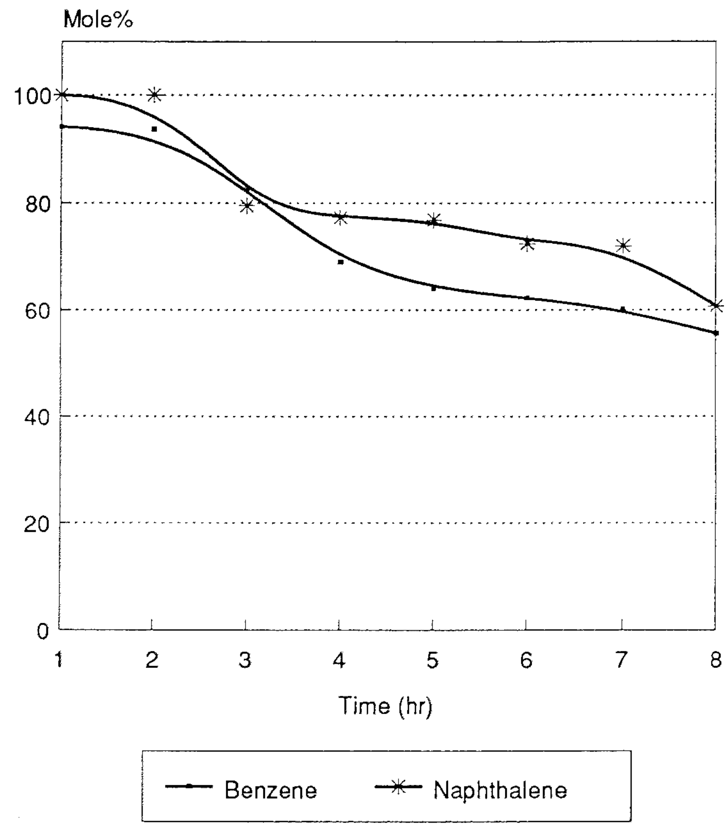


Figure 23. Change in benzene and toluene conversion with time Eight hour test using RE-2A



Run-F14-94

Figure 24. Change in benzene and naphthalene conversion with time. Eight hour test using RE-2A



Run-F14-94